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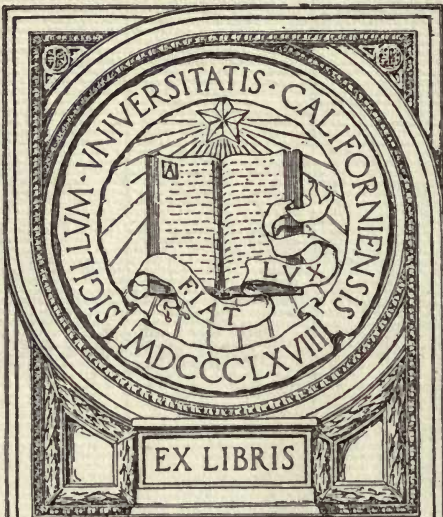
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# Influence of Certain Electrolytes ON THE Composition of Saturated Bredig Gold Sols

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## DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-  
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
IN THE FACULTY OF PURE SCIENCE IN  
COLUMBIA UNIVERSITY

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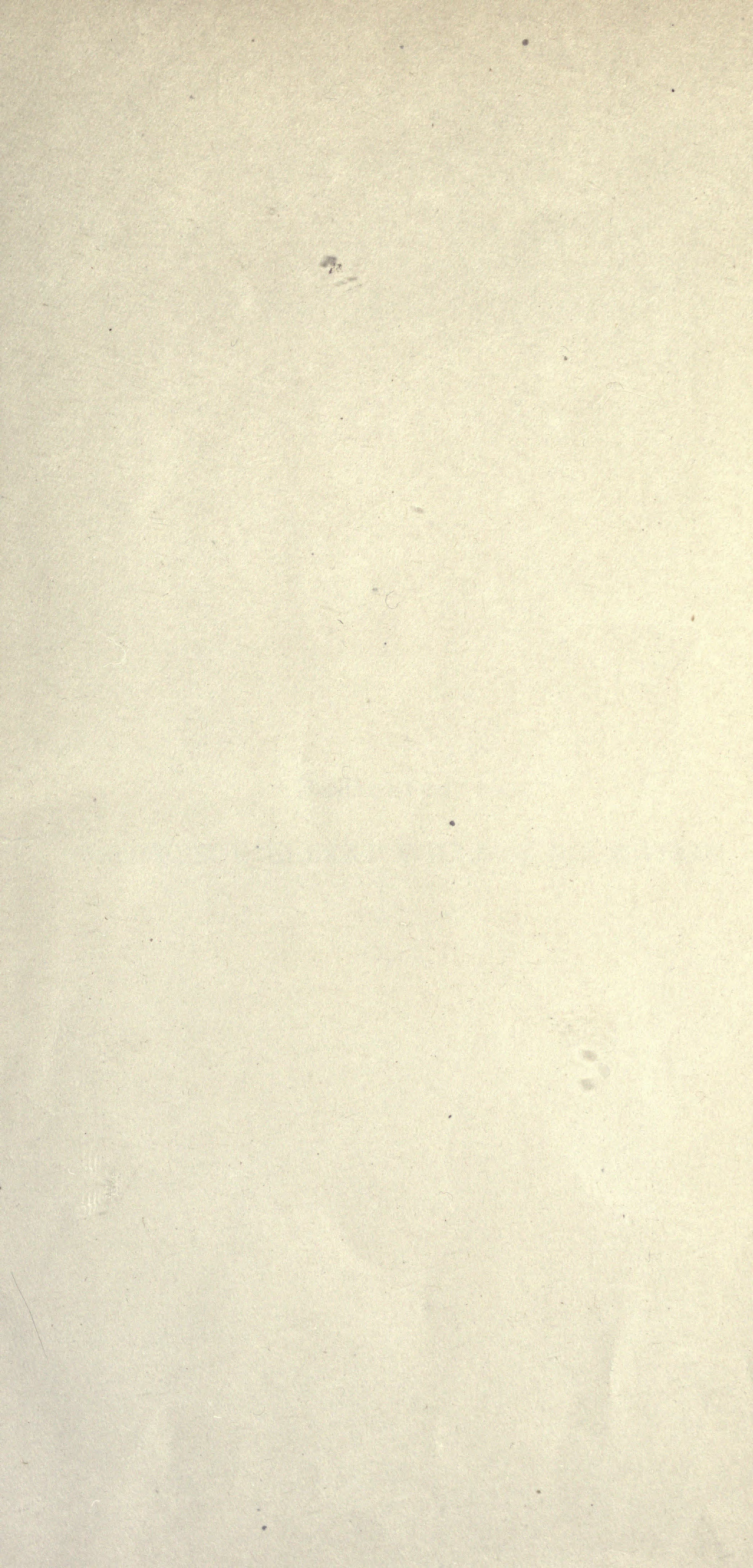
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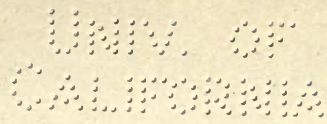
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#### ACKNOWLEDGMENT

The author wishes to express to Professor H. T. Beans his sincere thanks for the suggestion of the problem and for generous assistance and advice throughout the course of the investigation.

He also wishes to thank the other members of the Chemistry Department for their co-operation and assistance.

Exchange



# The Influence of Certain Electrolytes ON THE Composition of Saturated Bredig Gold Sols.

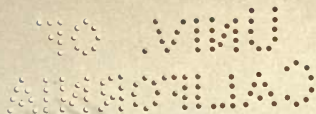
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## INTRODUCTION

The fact that certain colloidal dispersions were stable only in the presence of small amounts of electrolytes was first observed by Graham<sup>1</sup>, who found that ferric hydroxide and aluminium hydroxide sols could not be entirely freed from chloride, no matter how long the solutions were dialyzed. A great deal of work has since been done on these and other hydrosols showing that the presence of electrolyte is necessary to stabilize the colloid<sup>2</sup>.

The work of Picton and Linder<sup>18</sup>, Jordes and Kauter<sup>19</sup>, Lottermoser<sup>20</sup>, Svedberg<sup>21</sup>, and von Weimarn<sup>22</sup> has led to the development of the hypothesis that the particles of a hydrosol consists of a complex between a substance of very low solubility and an ion of an electrolyte, the presence of which is necessary to the stability of the sol and to which the sol particle owes its electrical charge.

While the application of this chemical or complex theory to inorganic hydrophilic dispersions has been general, hydrophobic dispersions, particularly those of the noble metals prepared by electrical dispersion, have been considered to be essentially different and to require no stabilizing electrolyte<sup>3</sup>. Bredig<sup>4</sup>, however, recommended the use of .001 N sodium hydroxide, while Whitney and Blake<sup>5</sup> state that "a more stable and more concentrated sol could be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a specific conductivity of  $200 \times 10^{-6}$  Mhos. That hydrophobic dispersions probably also require an electrolyte for their stabilization was indicated by the work of Beans and Eastlack<sup>5</sup>, who found that when carefully distilled water ("conductivity water") was used as the dispersion medium, stable gold sols could not be obtained by the Bredig method. The addition to the water of certain electrolytes in concentrations varying from



0.00005 to 0.005 normal resulted, however, in the formation of stable gold sols. Furthermore, that these sols were stabilized by the formation of some such complex as is assumed to be necessary in the case of hydrophilic dispersions was strongly indicated by the fact that only those electrolytes furnishing a negative ion capable of combining with gold to form a compound stable in aqueous solution are effective. And, finally, this work demonstrated that the complex is formed between the stabilizing ion and metallic gold since in all cases the solutions were found to be free from gold ion.

Beans and Beaver<sup>6</sup> found, in arcing gold electrodes in solutions of the nature and concentration described above, that the concentration of the dispersed gold increased with time of arcing up to a certain limit depending on the concentration of the electrolyte. If the process was continued beyond this limit the concentration decreased and the sol was entirely coagulated by a comparatively short period of arcing. They demonstrated also that centrifuging for one hour in a centrifuge capable of developing a force 1200 times gravity gave a sol of constant gold content. This shows that this force is inadequate to precipitate the colloidal particles, while it does remove the coarse suspended particles.

The important discovery of Beans and Beaver that the limiting concentration of gold in a Bredig sol depends upon the concentration of the electrolyte demanded quantitative study and it is the result of this investigation that forms the subject of this thesis.

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## APPARATUS AND MATERIALS USED

All solutions were made up in water having a specific conductivity of 1.46 to  $1.00 \times 10^{-6}$  imhos. The hydrochloric and hydrobromic acids were the constant boiling point acids prepared in quartz apparatus from Baker and Adamson's c. p. products. Baker's c. p. potassium chloride was twice re-crystallized from conductivity water and fused in a platinum dish. Baker's c. p. sodium chloride, potassium bromide, and potassium iodide were each re-crystallized three times from conductivity water and dried at  $110^\circ$  in a Freas electric oven. The cesium chloride was prepared from five times re-crystallized cesium nitrate, which gave no test for rubidium upon spectroscopic ex-

amination, by the method of H. L. Wells<sup>7</sup>. After purification the salt gave a negative test for iodine when a portion of it was shaken with chloroform, after acidifying with hydrochloric acid and adding a few drops of sodium nitrite. Kahlbaum's c. p. rubidium chloride, found to be spectroscopically free from cesium salts, was not further purified. Baker's c. p. lithium chloride was gently ignited in a platinum dish to remove water, dissolved in absolute alcohol and filtered to remove sodium and potassium chlorides. The alcoholic solution was then evaporated to dryness and gently ignited. The solution obtained by dissolving this product in water was acid to phenolphthalein. Sodium hydroxide solution, prepared from Eimer and Amend's c. p. product which was prepared from metallic sodium, was made up by filtering a saturated aqueous solution of the base through a dry filter paper, which separated all carbonate and chloride, and diluting with water.

All solutions were made up to approximately 0.02 molar concentration and standardized. The sodium hydroxide was standardized against Bureau of Standards pure benzoic acid. The hydrochloric and hydrobromic acids were standardized against the sodium hydroxide. Potassium chloride, bromide, and iodide, and the chlorides of sodium, rubidium and cesium were standardized by evaporating a definite volume to dryness in a weighed platinum dish, drying for several hours in an electric oven at 110°C, and finally igniting gently on an air bath, cooling and weighing. The lithium chloride was standardized by evaporating a definite volume of the solution in a platinum dish in the presence of an excess of sulphuric acid and finally igniting on an air bath, cooling and weighing as lithium sulphate.

The gold wire and arcing apparatus were the same as that used by Beans and Eastlack<sup>8</sup>, with the addition of a stirring device.

The centrifuge used for freeing the sols of coarse particles was a "type three centrifuge" of the International Equipment Co., with rotating arms two feet in diameter and with a speed 2000 r.p.m.

The burette, pipettes, volumetric flasks, and set of weights used were all standardized by the usual methods.

---

### METHOD OF PROCEDURE

All solutions for arcing were made up by diluting the

standard. The solution was then placed in a pyrex beaker and surrounded by an ice bath which kept the temperature in the neighborhood of  $25^{\circ}$  to  $30^{\circ}$  C. during the arcing, the solution being stirred vigorously by a glass stirrer connected to a motor. When the condition of saturation of the sol with respect to colloidal gold was approached, portions of the solution were removed at short intervals of time and placed in well steamed non-sol bottles. This was continued until the sol precipitated. The samples were then placed in glass centrifuge tubes and centrifuged for one hour at 1200 times gravity. A definite volume of the upper layer, free from coarse suspension particles, was then pipetted off carefully, precipitated with a few drops of hydrochloric acid, filtered through an ashless filter paper, burned and weighed in a porcelain crucible. A volume of sol was analyzed which yielded at least 50 milligrams of gold. From the highest value given by a set of samples the amount of gold in moles per liter was calculated.

Numerous points in each electrolyte were duplicated by making a fresh dilution from the standard and running the entire procedure again. In no case (except in sols prepared in cesium chloride solution) was the variation in the maximum quantity of gold determined by the two duplicates greater than two percent. of the total gold. In cesium chloride solutions, however, it was much more difficult to determine when the condition of saturation was being reached and some of the duplicates varied as much as five percent. from each other.

Potassium chloride was the first electrolyte to be tried and it was fairly completely investigated throughout the range for colloid stability. The zone of high concentrations for gold colloid seemed the more important and interesting, however, So in the remaining electrolytes the region of high concentration for gold was carefully investigated; the regions of low concentration, only in a general way.

In the following tables, obtained as outlined above, the concentration of electrolyte is expressed in mols per liter, the concentration of gold in atomic weights per liter.

TABLE I H Br

Conc. electro- lyte mols per litre.	Conc. Gold at. wt. per 1.
0.00020	0.0018
0.00050	0.0022
0.00080	0.0048
0.00100	0.0020
0.00110	0.0036
0.00120	0.0045
0.00130	0.0041
0.00150	0.0018
0.00180	0.0036
0.00200	0.0031
0.00220	0.0029
0.00250	0.0018

TABLE II K Br

Conc. electro- lyte mols per litre.	Conc. Gold at.wt. per 1.
0.00010	0.0046
0.00080	0.0086
0.00100	0.0103
0.00120	0.0162
0.00130	0.0146
0.00160	0.0102
0.00200	0.0053
0.00300	0.0028
0.00500	0.0006

TABLE III K Cl

Conc. electro- lyte mols per litre.	Conc. Gold at. wt. per 1.
0.0000125	0.0012
0.000025	0.0014
0.00005	0.0031
0.00010	0.0047
0.00060	0.0105
0.00100	0.0125
0.00120	0.0178
0.00130	0.0218
0.00140	0.0211
0.00160	0.0161
0.00200	0.0181
0.00230	0.0179
0.00250	0.0173
0.00300	0.0122
0.00500	0.0107
0.00650	0.0061
0.00800	0.0062
0.01000	0.0048
0.01200	0.0044
0.01500	slight
0.02000	none

TABLE IV H Cl

Conc. electro- lyte mols per litre.	Conc. Gold at.wt. per 1.
0.00010	0.0043
0.00060	0.0053
0.00100	0.0082
0.00110	0.0095
0.00120	0.0108
0.00130	0.0093
0.00140	0.0076
0.00180	0.0066
0.00200	0.0073
0.00220	0.0061
0.00300	0.0046
0.00500	0.0016

TABLE V Li Cl

Conc. electro- lyte mols per litre.	Conc. Gold at. wt. per 1.
0.00050	0.0125
0.00100	0.0178
0.00120	0.0213
0.00130	0.0225
0.00140	0.0210
0.00160	0.0205
0.00180	0.0203
0.00210	0.0202
0.00250	0.0206
0.00290	0.0210
0.00305	0.0207
0.00320	0.0209
0.00360	0.0201
0.00700	0.0172

TABLE VI Na Cl

Conc. electro- lyte mols per litre.	Conc. Gold at.wt. per 1.
0.00050	0.0140
0.00080	0.0165
0.00100	0.0175
0.00120	0.0182
0.00130	0.0258
0.00140	0.0206
0.00160	0.0176
0.00180	0.0216
0.00190	0.0203
0.00200	0.0201
0.00210	0.0222
0.00240	0.0204
0.00280	0.0191
0.00500	0.0107

TABLE VII Rb Cl

Conc. electro- lyte mols per litre.	Conc. Gold at. wt. per 1.
0.00050	0.0112
0.00100	0.0150
0.00110	0.0151
0.00120	0.0147
0.00130	0.0190
0.00150	0.0111
0.00170	0.0128
0.00180	0.0131
0.00220	0.0100
0.00260	0.0088
0.00700	0.0047

TABLE VIII Cs Cl

Conc. electro- lyte mols per litre.	Conc. Gold at.wt. per 1.
0.00060	0.0132
0.00080	0.0156
0.00090	0.0179
0.00095	0.0167
0.00100	0.0142
0.00105	0.0172
0.00110	0.0184
0.00115	0.0140
0.00120	0.0131
0.00130	0.0150
0.00135	0.0161
0.00140	0.0148
0.00150	0.0133
0.00170	0.0138
0.00200	0.0121
0.00400	0.0077

TABLE IX K I

Conc. electro- lyte mols per litre.	Conc. Gold at. wt. per 1.
0.00100	0.00013 very dilute purple sol.
0.00130	Dilute reddish, purple sol. Slightly more concen- trated than .001.
0.00150	Dilute reddish, purple sol.
0.00200	Very dilute purple sol. Above and below the above concentrations no sols, stable at 1200 times gravity, were formed.

The curves in figures I, II, and III were obtained by plotting the concentration of electrolyte expressed in mols per liter as ordinates against concentration of colloidal gold expressed in atomic weights per liter as abscissa.

These curves perhaps represent the resultant of two forces acting upon the gold particle, namely, the stabilizing effect of the negative ion and the precipitating effect of the positive ion. If we consider the stabilizing effect of the chloride ion to be a constant for the various alkali chlorides, then it is evident that the precipitating power of the cations increase in the following order, Li, Na, K, Rb, Cs, H. It is to be observed that this is the same order as the precipitating value<sup>10</sup> found for these ions when

electrolytes containing them are added to negative colloids to produce precipitation. It is also in the same order as the mobility<sup>9</sup> of the ions, which increase from lithium ion to hydrogen ion. It is the inverse order of the degree of hydration<sup>11</sup> of the ions and the ionic radii<sup>12</sup>. For the alkali metals this is also the same order as increase of atomic weights and metallic properties.

The stabilizing action of the negative ions decrease in the following order: chloride, bromide, and iodide. This is the same order as the decrease of precipitating power upon positively charged colloids when electrolytes containing these ions are added to the colloids<sup>13</sup>. It is also the same order as the decrease in ionic hydration<sup>11</sup>, non-metallic properties of the elements, and the stability of the corresponding gold halides. It is the inverse order for these ions of the stabilizing effect upon negative colloids<sup>14</sup> when electrolytes containing these ions are added to negatively charged colloids for the purpose of producing precipitation, and of the decrease of atomic weights. The ionic radii<sup>15</sup> and the mobilities<sup>16</sup> of the chloride, bromide, and iodide ions are nearly identical.

With the exceptions of the curves for hydrobromic acid and cesium chloride, the first and highest maximum point for gold concentration of each curve occurs at a concentration of electrolyte varying between 0.0012 and 0.0013 molar. For the two exceptions the second maximum occurs at these concentrations; the first maximum occurs between 0.0008 and 0.0009 molar concentration of electrolyte.

If we assume that there are two forces acting upon the colloid—the protective action of the ion of like charge to the colloid and the precipitating action of the oppositely charged ion, (Bredig gold sols are negatively charged)—then the peculiar character of the curves can be explained in one of the following ways:

(1) The negative ions possess a high stabilizing power through certain narrow ranges of concentration lying within the limits of concentration through which the colloids are stable. This results in the formation of one or more maxima when gold concentration is plotted against electrolyte concentration.

(2) The positive ions show a marked loss of precipitating power through certain narrow ranges.

(3) Or a combination of these two opposing actions occurs. The first hypothesis is supported by the fact that the maxima

FIG. I

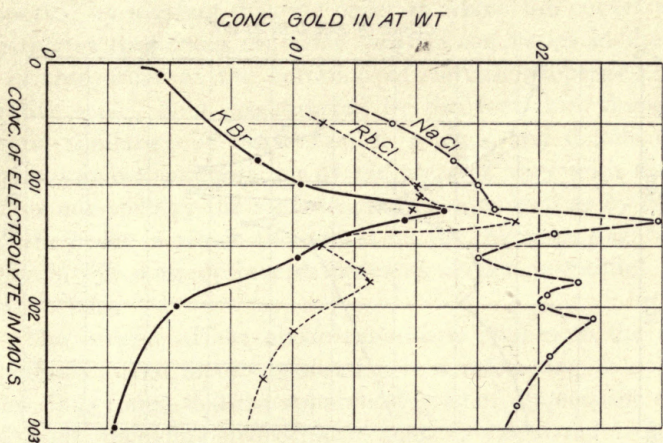
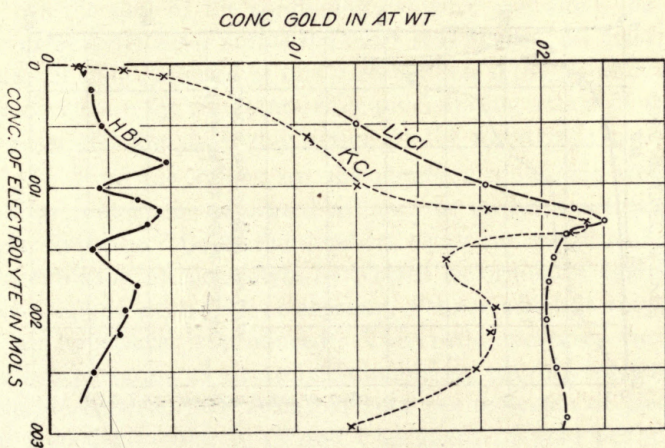
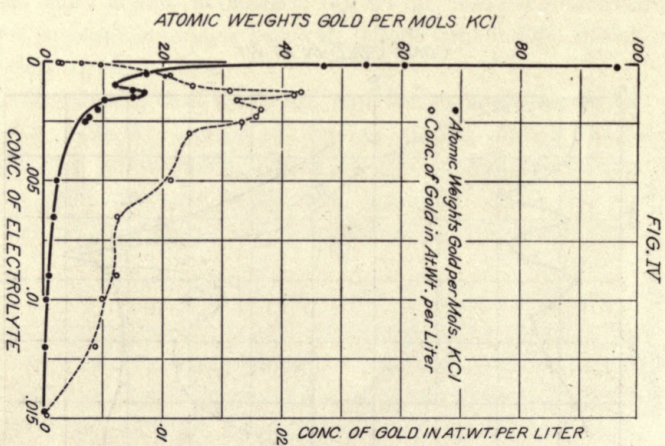
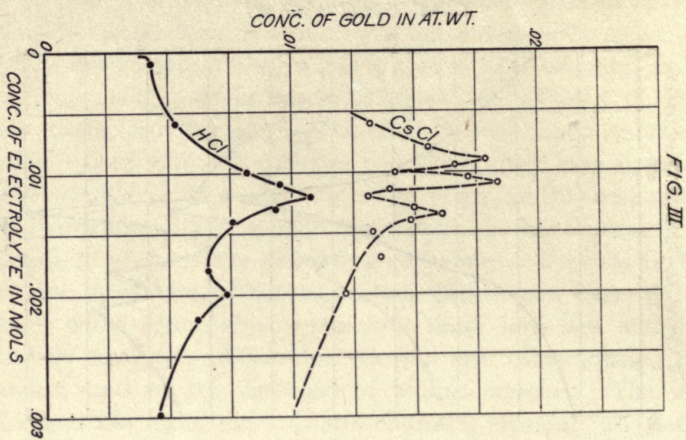


FIG. II





for the chlorides of hydrogen and of the alkali metals lie in the same general range of electrolyte concentration (.0012 — .0013 molar) and by the general similarity of the curves. It is further supported by the fact that the order in which the curves lie for electrolytes containing the same positive ion varies in the same or inverse order as the variation of certain properties of the negative ions. It is contradicted by the fact that, though the general similarity of the curves is evident, the details of the curves, number and location of the maxima vary with different compounds yielding the same negative ion, as well as by the fact that the order in which the curves lie for the same negative ion varies in the same or inverse order as certain properties of the positive ions.

The reverse of the above arguments applies to the second hypothesis. And in this connection it is interesting to note that Fales <sup>17</sup> has found that the apparent degree of dissociation of several acids, including hydrochloric acid, as calculated from electromotive force measurements by the hydrogen electrode reaches a maximum at about 0.001 normal concentration of the acids. This peculiarity, he thinks, may possibly be ascribed to hydration of the hydrogen ion. The concentration at which this maximum occurs is almost exactly the same as that at which the gold sols were in general found to be most stable.

In the face of the conflicting evidence just cited, the last of the three hypotheses seems the most reasonable. In brief, therefore, the data gathered in this investigation seems to indicate that the effects are the resultant of the precipitating action of the positive ion and the stabilizing action of the negative ion.

If, from the values for the numbers of atomic weights of gold present in the saturated sol and the molar concentration of electrolyte, the ratio of the numbers of atomic weights of gold to concentration of electrolyte be plotted as ordinates against concentration of electrolyte as abscissa, a curve which is very similar to an hyperbola is produced. This ratio increases rapidly as the concentration of electrolyte diminishes, varying for potassium chloride between 96.8 atoms of gold per molecule of electrolyte for 0.0000125 molar K Cl and 0.48 atoms of gold per molecule of electrolyte for 0.01 molar K Cl. In the absence of information as to whether all the chloride ions act as stabilizing units it is uncertain that this method of calculation is significant. It may, therefore, be taken as giving the minimum value for the average

number of atoms of gold which may be attached to a chloride ion in a saturated sol for each concentration of electrolyte.

The values obtained as described above have been plotted in Figure I, together with the complete saturation curve with respect to gold for that electrolyte. The data is given in Table X.

TABLE X

Mols of K Cl per liter	Atoms of gold per mol of K Cl
0.0000125	96.8
0.000025	54.4
0.00005	61.0
0.00010	47.4
0.00060	17.6
0.00100	12.5
0.00120	14.8
0.00130	16.8
0.00140	15.1
0.00160	10.0
0.00200	9.0
0.00230	7.8
0.00250	7.0
0.00500	2.1
0.00650	.9
0.00800	.8
0.01000	.5
0.01200	.36
0.01500	slight
0.02000	none

The efficiency of the arc in producing colloidal gold varied for different electrolytes; that is, the time of arcing in different electrolytes necessary to produce a sol containing a definite amount of colloidal gold varied considerably. For the chlorides the efficiency varied as follows: H or Li greater than Na greater than Rb greater than K or Cs. The efficiency in hydrogen or lithium chlorides was relatively twice as great as in potassium or cesium chlorides. The rate at which the gold electrodes were disintegrated was roughly of the same order. The efficiency also varied for different concentrations of the same electrolyte, being greatest in the more dilute solutions, and decreasing as the concentration of electrolyte increased.

Though nothing conclusive has been established as to the process by which colloidal dispersions are formed by the Bredig method, a study of the experimental results and conclusions of most of the previous investigators in this field points to the

process as being a purely thermo-mechanical one in which the metal is volatilized by the hot arc and then condensed by the cold dispersion medium to fine solid particles which remain suspended in the liquid. That the process was not as simple as this was indicated by the work of Beans and Eastlack<sup>5</sup> who showed that a definite kind and concentration of electrolyte was necessary to produce a stable colloidal suspension. The fact that the efficiency of the arc, kept under as constant conditions as possible, varies so greatly in different electrolytes points to the same conclusion. The work of Beans and Beaver<sup>6</sup> has shown that the stabilizing electrolyte is very definitely and strongly attached to the gold particle forming a complex which is not easily broken down by mechanical methods. The present work has shown that each concentration of electrolyte possesses a definite saturation value for gold under the conditions of formation, and that when this saturation value is exceeded the whole system becomes unstable. Each electrolyte which will stabilize gold has certain peculiar properties towards stabilization. All of these facts point to the conclusion that the process of formation is something more than a merely thermo-mechanical process.

To determine whether the curves represent the stability range of the colloids under all conditions or only for the conditions of preparation, the following experiments were performed: A 0.0013 molar solution of sodium chloride was prepared and arced until about four-fifths saturated with gold. It was then centrifuged and upon analysis was found to contain 4.070 grams of gold per liter (maximum value of gold found for this concentration of electrolyte is 5.088 grams per liter). A known volume of the centrifuged sol was placed in a steamed pyrex beaker which was then placed in a vacuum dessicator over sulfuric acid and allowed to evaporate slowly until the volume was reduced about half. By this process the concentrations of gold and electrolyte were so changed as to bring them above the region of stability as found. During the process long, very thin, yellow ribbons of gold formed on the surface of the sol and assumed a more or less feathery structure, appearing very much like crystals. Under the microscope they had the appearance of gold leaf and were so thin that light passed through them. A portion of the remaining solution was removed, centrifuged in the usual manner, the upper portion pipetted off and analyzed. It was found to contain 6.620 grams of gold per liter. This amount is greater

than the highest point on the sodium chloride curve by about thirty percent.

Secondly, a 0.0012 molar potassium bromide solution was prepared and arced until nearly saturated with gold. After centrifuging it was analyzed and found to contain 3.030 grams of gold per liter (maximum value of gold for this concentration of electrolyte is 3.204 grams per liter). Three parts of the centrifuged sol were then diluted with one part of water, placed in a well steamed non-sol bottle and allowed to stand for twenty-four hours. By diluting in this ratio the concentration of both gold and electrolyte were so changed as to bring them below the region of stability as found. After standing, the sol was again centrifuged and analyzed. It was found to contain 2.270 grams of gold per liter.

$$\frac{4}{3} \times 2.270 = 3.027$$

The sol is thus seen to contain, within experimental error of analysis, the same amount of gold per liter as before

From these experiments it is evident that the curves shown here represent the regions of stability for the formation of these sols under the experimental conditions described, but not for changes of concentration of either gold or electrolyte which may occur after the formation has taken place.

## SUMMARY

It has been shown that:

(1) In the preparation of gold sols by the Bredig method, there is a maximum amount of gold which can be stabilized by each concentration of electrolyte.

(2) One or more maxima occur in each curve produced by plotting concentration of gold against concentration of electrolyte.

(3) The first and highest maximum point occurs at a concentration of electrolyte of 0.0012 to 0.0013 molar with two exceptions.

(4) The curves represent the regions of stability for the formation of these sols but not for subsequent changes of concentration which these sols may undergo.

(5) The process of formation of Bredig gold sols cannot be purely thermo-mechanical.

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<sup>18</sup>*J. Chem. Soc.* 61. (1892) 114; 87, (1905) 1906.

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<sup>22</sup>*Kolloid Z.*, 2, (1907) 142.

<sup>23</sup>For a summary of this work see Beans and Eastlack, *J.A.C.S.* 37, 2667; and Makhopadhyaya, *J.A.C.C.*, 37, 292.

### *V I T A*

Lewis Benjamin Miller was born near Parkersburg, Iowa, on June 24, 1896, and attended the grade and high schools of that city. He received the degree of B.A. from the State University of Iowa, Iowa City, Iowa, in June, 1919. He attended the graduate school at that place from June, 1919, until August, 1920, at which time he received the degree of M.S. During the three years 1918 to 1920 he was Assistant in Chemistry at the State University of Iowa. From September, 1920, until the present he has attended the graduate school of Columbia University. He was laboratory assistant in Inorganic Chemistry from September, 1920, till June, 1921, and Assistant in Chemistry from July, 1921, until the present.



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